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(54) Title: OPTICAL MEDIA COMPRISING POLYMERIC MATERIAL FILM

(57) Abstract: An optical media comprising a polymeric material film, wherein said polymeric material is a polyester obtained from a 9,9-bis(4-hydroxyphenyl)fluorene derivative and a mixture of terephthalic acid and isophthalic acid derivatives, said polymeric material having an inherent viscosity lower than 0.80 dl/g and a yellowing coefficient Yc lower than 0.0050.



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The International Bureau is respectfully requested to record the change of the name and address of the applicant appearing on the request of the subject international application from

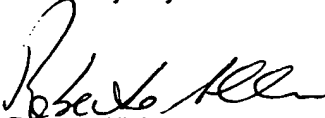
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Yours very truly.


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TITLE

Optical Media Comprising Polymeric Material Film

FIELD OF THE INVENTION

The present invention relates to an optical media comprising an high quality
5 polymeric material film. More in particular, the present invention relates to an optical
media comprising a polymeric material film having resistance to ageing and UV radiation.

BACKGROUND OF THE INVENTION

Flat-panel displays (FPD) are becoming increasingly commonplace in today's
commercial electronic devices. FPD in most of their applications are expected to be
10 lightweight, portable, rugged, low-power and high-resolution. Displays having all these
attributes will enable a wide variety of commercial applications in the future.

Most commercially available products use glass as the starting material in the
display fabrication process. Glass has been widely used for several optical applications,
due to its excellent characteristics, such as the transparency, the optical clarity, the high
15 transparence in the visible light range, the high resistance to temperature and the
compatibility with chemicals used in standard semiconductor manufacturing processing.
Notwithstanding, due to its high weight and high brittleness, the use of glass as support in
optical applications may cause problems to the final product realization. In addition,
because glass is not flexible, it cannot be used in continuous processing, this leading to a
20 relatively low final productivity.

In view of these reasons, it should be desirable to replace glass with transparent
plastic films. If plastic is employed as the starting material for display manufacturing, a
display that is not only lightweight and rugged but also flexible can be obtained. The
realization of such a technology would have a significant impact on the display industry
25 replacing the present sheet processes with a continuous roll-to-roll manufacturing
process.

The actual process involved in the display manufacturing are designed to work
with the glass support that has excellent thermo-mechanical and optical properties and
that can withstand high temperature processes, solvent treatments and UV-visible light
30 exposure without significant changes in its properties.

Typical display manufacturing processes, such as those to manufacture liquid
crystal display (LCD) and organic light emitting diode (OLED), having an active matrix
(AM) or a passive matrix (PM), use the glass as support, at present. The glass is the
starting point for the manufacturing process which comprises the coating of different
35 functional layers which can vary according to the desired kind of display. Metals or metal
oxides such as silicon or indium tin oxide (ITO) are coated on the glass by sputtering or
vacuum deposition, for instance, and then treated by thermal, laser or chemical treatment
to form the driving circuit of the display. In case of high performance driving circuits (TFT,

for example) these processes are carried out on glass at a temperature of about 600°C. Recent developments have reduced this temperature to about 250-350°C by laser technique.

Most of the plastic materials available in the market, in spite of having optical
 5 properties that match the requirements for applications as support for display, have glass transition temperature lower than 240°C and this make them useless in the above mentioned processes. US 5,817,550 and US 5,856,858 describe a method for the formation of thin film transistors on low-temperature plastic substrates. The methods includes the substrate to be coated on both sides by 0.1-5.0 microns of SiO₂ as first step
 10 in the manufacturing process. This allow the film to withstand the high temperature required by the TFT assembly. N.D. Young et Al., Low Temperature Poly-Si on Glass and Polymer Substrates, ASIA DISPLAY Workshop, 1998 describe the fabrication of polycrystalline silicon TFT on polymer supports. Thermal stability up to 250-350°C is required to the polymer substrate in order to obtain TFT's circuits with good properties,
 15 such as high mechanical properties and low thermal shrinkage rate to guarantee a good stability and self-sustaining properties during the construction processes. Further, protective layers are needed to increase the resistance to chemicals and solvents during displays manufacturing steps.

High mechanical properties are needed to obtain a self-supporting film during the
 20 device assembly and its use. Eventually, a good resistance to the UV-visible light exposure without remarkable degradation (support embrittlement and colour changes) is required to withstand the process steps where UV sources can be used and to prevent degradation in sunlight environment applications.

Other problems are related to the stability during time of the displays. Active
 25 materials used in displays are extremely sensitive to oxidation and then to the presence of oxygen and moisture in the internal side of the displays. High barrier properties against said oxygen and moisture The glass accordingly provides a suitable impermeability level for this kind of applications, while, on the contrary, the plastic generally is too permeable. This problem, together with the resistance to chemicals and scratches is solved by adding
 30 suitable functional layers to the surface of the plastic film. Most common anti-scratches layers and barrier layers are based on UV-photocurable materials and this makes the substrate UV resistance one of the main required properties for the potential plastic support for optical devices. US 6,358,570, US 6,268,695 and US 6,413,645 disclose barrier layers coated on the plastic film. The main application is as plastic support for
 35 displays where high barrier properties to moisture and oxygen are required. The barrier structure is a multilayered composition of curable resins and inorganic compounds. The resins can be cured by UV radiation.

Several patents and patent applications describe fluorene polyester materials for electrical applications.

US Patent 3,546,165 describes thermally stable polyesters of various gem-bisphenols and dicarboxylic acids. Included are polyesters of 9,9-bis(4-hydroxyphenyl)fluorene with 100% isophthalic acids and 9,9-bis(4-hydroxyphenyl)fluorene with 80%wt isophthalic acid and 20%wt terephthalic acids. Softening temperature of 360°C for both these polymers are reported. UV stability and mechanical properties have not been evaluated.

US Patent 4,387,209 describes polyesters made by reacting 9,9-bis-(4-hydroxyphenyl)-fluorene with at least one member of the group consisting of isophthalic or terephthalic acid and using an interfacial polymerization process. The polyester inherent viscosity strongly depends upon the monomer purity and relatively small variations in purity of the diphenol monomer may cause large deviations in the inherent viscosity values. Polyester films are described to be used in the electrical insulation field, and neither data on optical properties nor possible applications are reported.

US 4,967,306 discloses a 9,9-bis-(4-hydroxyphenyl)-fluorene/isophthalic and terephthalic acid polyester which contains a very low level of low molecular weight oligomers and has a tensile strength, elongation, chemical resistance, temperature stability, ultraviolet resistance and vacuum stability higher than the known in the art copolymers containing low molecular weight oligomeric species. It is disclosed therein that films containing small amounts of oligomer will yellow or degrade upon limited exposure to ultraviolet radiation.

The resin obtained from the polyarylate composed of 9,9-bis-(3-methyl-4-hydroxyphenyl)-fluorene and isophthalic acid reported in Journal of Applied Polymer Science, Vol. 29, p. 35 to 43 (1984) results to be too fragile and has insufficient abrasion resistance and low film quality.

Japanese Patent Application No. 09-071,640 discloses a resin composed of (a) an aromatic dicarboxylic acid, (b) a specific amount of a substituted 9,9-bis-(4-hydroxyphenyl)-fluorene and (c) an aliphatic glycol; said resin is utilized in optical materials for its good transparency and heat resistance.

US 4,810,771 discloses polyesters made of mono-ortho substituted bisphenols, and a blend of isophthalic and terephthalic acid.

EP Patent Application 943,640 describes a film prepared with polyarylates synthesized using bisphenolfluorenes mono- and bi-substituted in the ortho position with alkyl (C1-C4) groups. Such polyarylates have a better stability to ultraviolet radiation.

9,9-bis(3,5-dibromo-4-hydroxyphenyl)-fluorene bisphenol monomer derived polyarylates have been disclosed in PCT Patent Application No. WO 00-33,949 as gas-separation membranes.

In US 5,007,945, there is described a polyarylate class obtained from dicarboxylic acid chlorides and cardo bisphenols having halo-substituents on all ortho positions of the phenol groups, which is used to separate one or more components of a gas mixture. Such patents describe gas-separation membranes, but do not mention optical films consisting of such polymers.

The present invention describe a plastic film suitable for optical applications and more preferably as a display support, able to withstand to the present manufacturing processes and to the environmental conditions during its use. Also, the use of a flexible plastic support will allow to introduce roll-to-roll technologies in the manufacturing of displays.

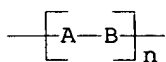
SUMMARY OF THE INVENTION

An optical media comprising a polymeric material film, characterized in that said polymeric material is a polyester obtained from a 9,9-bis(4-hydroxyphenyl)fluorene derivative and a mixture of terephthalic acid and isophthalic acid derivatives, said polymeric material having an inherent viscosity lower than 0.80 dl/g and a yellowing coefficient Yc lower than 0.0050.

DETAILED DESCRIPTION OF THE INVENTION

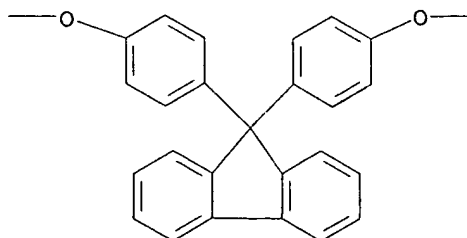
An optical media comprising a polymeric material film, characterized in that said polymeric material is a polyester obtained from a 9,9-bis(4-hydroxyphenyl)fluorene derivative and a mixture of terephthalic acid and isophthalic acid derivatives, said polymeric material having an inherent viscosity lower than 0.80 dl/g and a yellowing coefficient Yc lower than 0.0050.

The polyester useful in the present invention can be represented by the general structure:



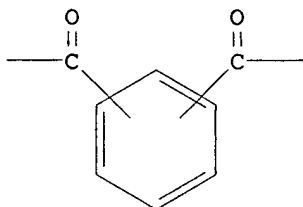
wherein

A represents one or more different 9,9-bis(4-hydroxyphenyl)fluorene group having general formula (I):



formula (I)

B represents one or more different dicarboxy groups having the formula:

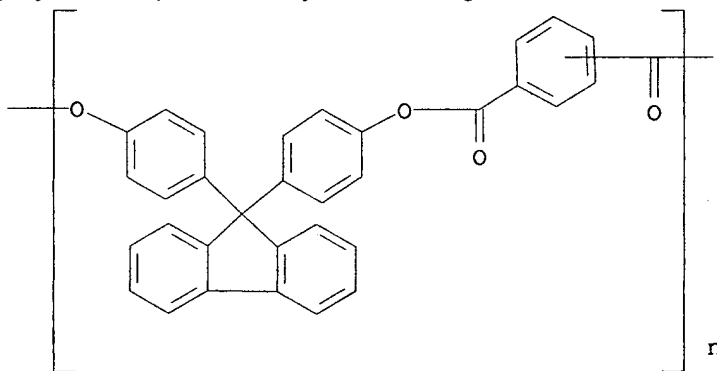


formula (II)

and

n is the number of the repeating units which build up the polymer and is a positive integer higher than 20.

Preferably, the present invention refers to an optical film comprising one or more polyesters represented by the following structure:



wherein n is a positive integer higher than 20. Still more preferably, the present invention refers to an optical film comprising a polyester obtained from at least two different polymerizable units represented by the 9,9-bis-(4-hydroxyphenyl)-fluorene group of general formula (I) and from a mixture of isophthalic acid and terephthalic acid. The mixture of isophthalic acid and terephthalic acid preferably comprises from 10 to 90% by weight of an isophthalic group and from 90 to 10% by weight of a terephthalic group; more preferably, the mixture of isophthalic acid and terephthalic acid comprises from 20 to 80% by weight of an isophthalic group and from 80 to 20% by weight of a terephthalic group; most preferably, the mixture of isophthalic acid and terephthalic acid comprises from 30 to 70% by weight of an isophthalic group and from 70 to 30% by weight of a terephthalic group.

When in the present invention the term "group" is used to describe a chemical compound or substituent, the described chemical material comprises the group, ring and base residue and that group, ring or residue with conventional substituents. When on the contrary the term "unit" is used, on the un-substituted chemical material is intended to be included. For instance, the term "alkyl group" comprises not only those alkyl units, such as methyl, ethyl, butyl, octyl, etc., but also those units bearing substituents such as

halogen, nitrile, hydroxy, nitro, amino, carboxy, etc. The term "alkyl unit" on the contrary comprises only methyl, ethyl, cyclohexyl, etc.

The polymeric material useful in the present invention has excellent resistance to ageing and to UV radiation and is less subject to yellowing upon exposure to UV-visible
 5 light sources. More in particular, the polymeric material shows a inherent viscosity lower than 0.80 dl/g, preferably lower than 0.70 dl/g, and more preferably in the range of from 0.65 to 0.30 dl/g.

The polymeric material of the present invention can replace glass support in the manufacturing of a number of optical media known in the art, such as liquid crystal
 10 displays, electroluminescent displays, organic light-emitting diode displays, and the like. This allows to obtain more flexible and resistant displays than those conventionally manufactured using glass supports. Also, the use of the polymeric material of the present invention allows to use roll-to-roll technologies in the manufacturing of displays.

EXAMPLES

15 Sample films were obtained by taking compound A and polymerizing it with the interfacial polycondensation technique as described in EP patent 396,418, utilizing a mixture of terephthalic acid (TPA) and isophthalic acid (IPA) and obtaining different inherent viscosity values as reported in the following Table 1. The so-obtained polymer
 20 was coated with the solvent coating technique using a 10% weight methylene chloride solution of the polymer. The resulting film having a thickness of 100 μm was then dried for 3 hours at a temperature of 25°C, gradually increasing the temperature up to a maximum of 160°C. The inherent viscosity of each sample was measured with a viscosimeter SCHOTT GERATE AVS400 equipped with bath thermal control HAAKE D8 and a capillary-viscometer SCHOTT Ubbelohde 53113 Ic. Viscosity has been evaluated for
 25 solution of 0.1000 g dry polymer in 50ml of a mixture of phenol/1,1,2,2-tetrachloethane 60/40 % by wt. The data related to inherent viscosity of each sample are reported in the following Table 1.

TABLE 1

Sample film	% TPA	% IPA	Inherent Viscosity dl/g
1 (comparison)	50	50	2.12
2 (invention)	0	100	0.77
3 (comparison)	100	0	0.94
4 (invention)	50	50	0.31
5 (invention)	0	100	0.42
6 (invention)	100	0	0.63

Film samples were then subjected to UV ageing tests by using a Fusion F300 Lamp System produced by Fusion UV Systems Inc. equipped with a D bulb.

Sample film yellowing was measured by comparing their absorbance, before and after the expositions, at the selected wavelength of 400nm which was identified as the most significant (blue light absorption). Optical absorbance was measured by a Perkin-Elmer Lambda 2 spectrophotometer working in the 320-500 nm range. The Yellowing Coefficient (Yc) is defined as the ratio of the averaged variation of absorbance of a polymeric film exposed to a UV radiation source and the effective exposure energy. The exposure energy employed was up to 5.0 J/cm². The lower the value, the best the result.

The results were summarized in the following Table 2.

TABLE 2

Sample	Yellowing Coefficient Yc
1 (comparison)	0.0059
2 (invention)	0.0031
3 (comparison)	0.0069
4 (invention)	0.0043
5 (invention)	0.0013
6 (invention)	0.0047

The data of Table 2 showed that good or optimal values (i.e., lower than 0.0050) of Yellowing Coefficient can be obtained with film samples of the present invention having a inherent viscosity lower than 0.80 dl/g.

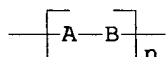
While a particular embodiment has been set forth to exemplify and explain the principles of the invention, such are not intended to be limiting. Modifications and changes may become apparent to those skilled in the art, and it is intended that the invention be limited only by the scope of the appended claims.

CLAIMS

1. An optical media comprising a polymeric material film, characterized in that said polymeric material is a polyester obtained from a 9,9-bis(4-hydroxyphenyl)fluorene derivative and a mixture of terephthalic acid and isophthalic acid derivatives, said
5 polymeric material having an inherent viscosity lower than 0.80 dl/g and a yellowing coefficient Yc lower than 0.0050.

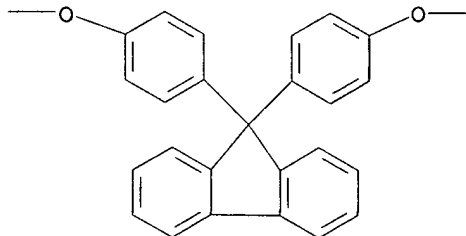
2. The optical media according to claim 1, characterized in that said polymeric material having an inherent viscosity lower than 0.70 dl/g.
10

3. The optical media according to claim 1, characterized in that said polyester is represented by the general structure:



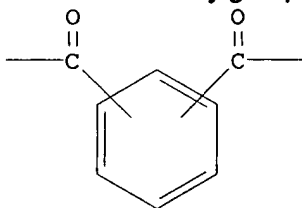
15 wherein

A represents one or more different 9,9-bis(4-hydroxyphenyl)fluorene group having general formula (I):



formula (I)

B represents one or more different dicarboxy groups having the formula:



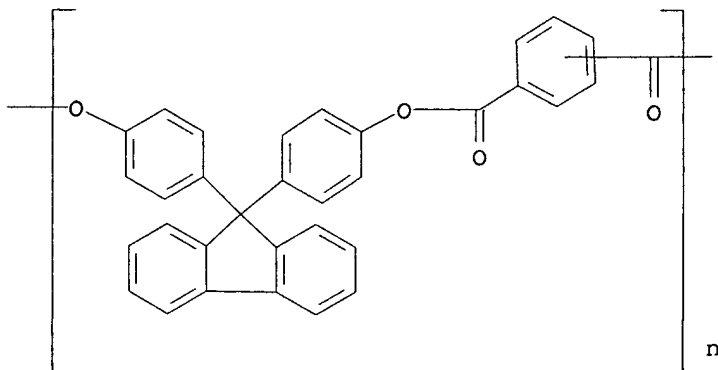
formula (II)

and

n is the number of the repeating units which build up the polymer and is a positive integer higher than 20.

25

4. The optical media according to claim 1, characterized in that said polyester is represented by the following structure:



wherein n is a positive integer higher than 20.

5. The optical media according to claim 1, characterized in that said polyester is
 5 obtained from 9,9-bis(4-hydroxyphenyl)fluorene and a mixture of terephthalic acid and
 isophthalic acid.

6. The optical media according to claim 5, characterized in that said mixture of
 terephthalic acid and isophthalic acid comprises from 20 to 80% by weight of an
 10 isophthalic group and from 80 to 20% by weight of a terephthalic group.

7. The optical media according to claim 5, characterized in that said mixture of
 terephthalic acid and isophthalic acid comprises from 30 to 70% by weight of an
 isophthalic group and from 70 to 30% by weight of a terephthalic group.

15

ABSTRACT OF THE INVENTION

An optical media comprising a polymeric material film, wherein said polymeric material is a polyester obtained from a 9,9-bis(4-hydroxyphenyl)fluorene derivative and a mixture of terephthalic acid and isophthalic acid derivatives, said polymeric material
5 having an inherent viscosity lower than 0.80 dl/g and a yellowing coefficient Yc lower than 0.0050.

INTERNATIONAL SEARCH REPORT

International Application No. PCT/EP2004/003581

A. CLASSIFICATION OF SUBJECT MATTER IPC 7 C08G63/193 C08J5/18 G02B1/04				
According to International Patent Classification (IPC) or to both national classification and IPC				
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC 7 C08G C08J G02B				
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched				
Electronic data base consulted during the international search (name of data base and, where practical, search terms used) EPO-Internal, WPI Data				
C. DOCUMENTS CONSIDERED TO BE RELEVANT				
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.		
X	US 5 115 372 A (HAMPL JR EDWARD F ET AL) 19 May 1992 (1992-05-19) abstract column 2, line 58 - column 3, line 33 column 5, line 37 - line 46 column 6, line 39 - line 49; claims; examples	1-7		
X	DATABASE WPI Section Ch, Week 199721 Derwent Publications Ltd., London, GB; Class A23, AN 1997-231217 XP002288584 & JP 09 071640 A (TOYOCO KK) 18 March 1997 (1997-03-18) cited in the application abstract; claims examples	1,2,5-7		
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<table style="width: 100%; border: none;"> <tr> <td style="width: 50%; border: none;"> <input checked="" type="checkbox"/> Further documents are listed in the continuation of box C. </td> <td style="width: 50%; border: none;"> <input checked="" type="checkbox"/> Patent family members are listed in annex. </td> </tr> </table>			<input checked="" type="checkbox"/> Further documents are listed in the continuation of box C.	<input checked="" type="checkbox"/> Patent family members are listed in annex.
<input checked="" type="checkbox"/> Further documents are listed in the continuation of box C.	<input checked="" type="checkbox"/> Patent family members are listed in annex.			
<table style="width: 100%; border: none;"> <tr> <td style="width: 50%; border: none; vertical-align: top;"> * Special categories of cited documents : *A* document defining the general state of the art which is not considered to be of particular relevance *E* earlier document but published on or after the international filing date *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) *O* document referring to an oral disclosure, use, exhibition or other means *P* document published prior to the international filing date but later than the priority date claimed </td> <td style="width: 50%; border: none; vertical-align: top;"> *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. *G* document member of the same patent family </td> </tr> </table>			* Special categories of cited documents : *A* document defining the general state of the art which is not considered to be of particular relevance *E* earlier document but published on or after the international filing date *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) *O* document referring to an oral disclosure, use, exhibition or other means *P* document published prior to the international filing date but later than the priority date claimed	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. *G* document member of the same patent family
* Special categories of cited documents : *A* document defining the general state of the art which is not considered to be of particular relevance *E* earlier document but published on or after the international filing date *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) *O* document referring to an oral disclosure, use, exhibition or other means *P* document published prior to the international filing date but later than the priority date claimed	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. *G* document member of the same patent family			
Date of the actual completion of the international search <div style="text-align: center; font-weight: bold;">15 July 2004</div>	Date of mailing of the international search report <div style="text-align: center; font-weight: bold;">29/07/2004</div>			
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fac. (+31-70) 340-3016	Authorized officer <div style="text-align: center; font-weight: bold;">Masson, P</div>			

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP2004/003581

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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